Short communication

Direct peroxide–peroxide fuel cell – Part 2: Effects of conditions on the performance

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HIGHLIGHTS

► A high performance direct peroxide–peroxide fuel cell (DPPFC) is demonstrated.
► The Pd/CFC electrode is a good catalyst for the anode and cathode reactions.
► The DPPFC displays a peak power density of 14.3 mW cm^{-2} at 20 °C.

ARTICLE INFO

ABSTRACT

A high performance direct peroxide–peroxide fuel cell using dendritic Pd supported on carbon fiber cloth as both the anode and the cathode is reported. Effects of the concentration of H_2O_2, KOH, H_2SO_4, the operating temperature and the flow rate on the fuel cell performance are investigated. The cell exhibits a much higher performance than those reported in the literature. The open circuit voltage reaches 0.9 V and the peak power density is as high as 14.3 and 58.4 mW cm^{-2} at 20 °C and 60 °C, respectively, when running on 4.0 mol L^{-1} KOH + 1.0 mol L^{-1} H_2O_2 as the fuel and 2.0 mol L^{-1} H_2SO_4 + 2.0 mol L^{-1} H_2O_2 as the oxidant, both at a flow rate of 10 mL min^{-1}.

1. Introduction

Studies on direct liquid peroxide–peroxide fuel cell (DPPFC), with H_2O_2 electrooxidation at the anode and H_2O_2 electroreduction at the cathode, have become frequently reported recently [1–5]. Comparing with other types of liquid-based fuel cells, such as the direct methanol fuel cell (DMFC) [6–10], the direct formic acid fuel cell (DFAFC) [11–17] and the direct borohydride fuel cell (DBFC) [18–23], the DPPFC has many advantages including: (1) The products from electrooxidation and electroreduction of H_2O_2 are only O_2 and H_2O, which are environmentally friendly. (2) The electrochemical oxidation and reduction of H_2O_2 involve no intermediates or by-products that can cause catalysts poisoning. (3) In DPPFC, H_2O_2 crossover is not a problem because H_2O_2 is both the

fuel and the oxidant. (4) The electrooxidation of H_2O_2 is a simple two-electron transfer process and has lower activation energy than the electrooxidation of methanol (six-electron transfer process) [6,8,9] and the electrooxidation of BH_4^- (eight-electron transfer process) [18,20]. The electroreduction of H_2O_2 has faster kinetics than oxygen reduction. (5) H_2O_2 is less toxic than methanol, formic acid, borohydride, and hydrazine. (6) The total cost of the energy production by DPPFC (1.84 \$/kW) may be more competitive than DMFC (6 \$/kW) and DBFC (10.2 \$/kW) [4].

In recent years, studies on DPPFC have made slow progress. Hasegawa et al. [1] and Chang and coworkers [2] first reported a H_2O_2 fuel cell in which H_2O_2 functions both as a fuel and an electron acceptor. Later on, Yamazaki et al. [3] reported a one-compartment H_2O_2 fuel cell, which exhibited a maximum current density of 2.9 mA cm^{-2} and an open circuit voltage of around 100 mV. Very recently, Sanli et al. [4,5] reported a two-compartment H_2O_2 fuel cell having the conventional fuel cell configuration. By using Ni as the anodic catalyst with basic H_2O_2 as

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fuel, Pt as the cathodic catalyst with acidic H_2O_2 as oxidant, they achieved a peak power density of 3.8 mW cm^{-2} and an open circuit voltage of around 0.9 V. However, the performance of the DPPFC is still considerably lower than that of other types of fuel cell.

We have successfully fabricated a novel electrode by depositing dendritic Pd particles onto carbon fiber cloth (Pd/CFC) (Part 1 of this series) [24]. The electrode exhibited high catalytic activity and stability for H_2O_2 electrooxidation in alkaline electrolyte and electroreduction in acid electrolyte. As an ongoing of this study, we report the performance of a DPPFC using this novel Pd/CFC electrode as both the anode and cathode. We demonstrated that such a DPPFC displayed a significantly higher performance than that reported in the previous literature.

2. Experimental

2.1. Preparation of the Pd/CFC electrode

The detailed preparation and characterization of the Pd/CFC electrode can be found in Ref. [24]. Briefly, the Pd/CFC electrodes were prepared by potential pulse electrodeposition of Pd onto CFC in 5.0 mmol L^{-1} PdCl$_2$ + 0.1 mol L^{-1} HClO$_4$ solution. The upper potential (E_U) was 0.5 V and the lower potential (E_L) was −0.1 V. The frequency of potential wave is 100 Hz and deposition time is 20 min. The depositions were carried out in a three-electrode electrochemical cell controlled by a potentiostat (Autolab PGSTAT302, Eco Chemie). The CFC (1.0 × 1.0 cm) served as the working electrode, which was placed between two pieces of platinum foil (1.0 × 1.0 cm) in parallel as the counter electrodes. A saturated Ag/AgCl (3.0 mol L^{-1} KCl) electrode was used as the reference electrode. The obtained Pd/CFC electrode has a Pd loading of 0.3061 mg cm^{-2}.

2.2. Direct H_2O_2–H_2O_2 fuel cell tests

The schematic representation of the configuration of DPPFC is shown in Fig. 1. As indicated by the anode and cathode reactions, during the fuel cell operation, OH$^-$ reacts H_2O_2 resulting in the increases of K$^+$ concentration in the anode compartment (positive charge in excess). At the cathode side, H$^+$ reacts with H_2O_2 leading to the increase of SO$_4^{2-}$ concentration (negative charge in excess). In order to balance the charge, K$^+$ will migrate from the anode to the cathode though the Nafion® membrane (DuPont de Nemours, Wilmington, DE., USA). So K$^+$, instead of H$^+$, is the migrating cation. It is worth to point out that, in this type of fuel cell, KOH and H_2SO_4
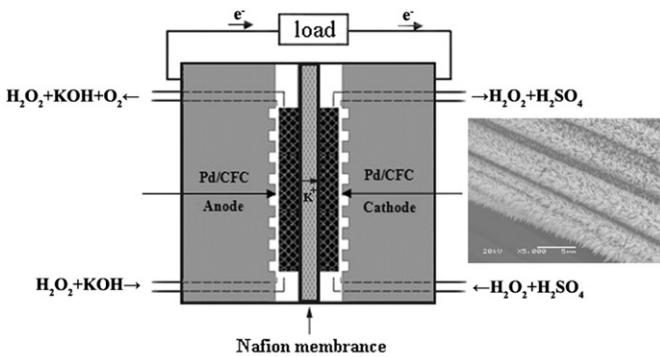
are the reactants. They take part in the anode and cathode reactions. Nafion® membrane works as the electrolyte to transport K$^+$.

Both the anode and cathode were the Pd/CFC electrodes, which were prepared by electrodeposited of dendritic Pd onto carbon fiber cloth via a potential pulse technique [24]. Nafion® 115 membrane was used to separate the anode and cathode compartments. The membrane was pretreated by boiling in 3% H_2O_2 for 1 h, in 0.5 mol L^{-1} H_2SO_4 for 2 h and in ultrapure water for 2 h prior to use. The membrane electrode assembly (MEA) was fabricated by hot-pressing the anode and cathode onto each side of the Nafion-115 membrane at 135 °C for 60 s. The active area of the Pd/CFC electrode was 5 cm^2 with a Pd loading of 0.3061 mg cm^{-2}. The prepared MEA was sandwiched between two graphite plates with a serpentine flow field. The anolyte (a solution of KOH and H_2O_2) and the catholyte (a solution of H_2SO_4 and H_2O_2) were pumped into the bottom of the anode and the cathode compartments, respectively, by two individual peristaltic pumps and exited at the top of the compartments. The anolyte and catholyte were circulated during the cell test. The discharge performance of the DPPFC was measured using a computer-controlled E-load system (Arbin, USA).

3. Results and discussion

3.1. Effects of anolyte composition

In Part 1 of this series [24], we systemically studied the effect of the concentration of H_2O_2, KOH and H_2SO_4 on the catalytic performance of Pd/CFC electrode for H_2O_2 electrochemical oxidation or reduction. It was found that the Pd/CFC electrode exhibited a higher catalytic activity for H_2O_2 electrooxidation in alkaline electrolyte than electroreduction in acid electrolyte. KOH and H_2SO_4 in excess show no improvement to the activity of H_2O_2 oxidation and reduction, respectively. In the present work, we studied the effects of KOH, H_2SO_4 and H_2O_2 concentration, operating temperature, and flow rate on the performance of the DPPFC using the H_2O_2 + KOH solution as the fuel, the solution of H_2O_2 + H_2SO_4 as the oxidant and the Pd/CFC electrode as the anode and the cathode.

Fig. 2 shows the effects of KOH concentration in the anolyte on the cell performance. The concentration of H_2O_2 in the anolyte was kept at 1.0 mol L^{-1} with the concentration of KOH varied from 2.0 to 6.0 mol L^{-1}. The catholyte was 2.0 mol L^{-1} H_2SO_4 + 2.0 mol L^{-1} H_2O_2

Fig. 1. A schematic representation of the direct H_2O_2–H_2O_2 fuel cell configuration.

Anode: $H_2O_2 + 2KOH \rightarrow O_2 + 2H_2O + 2K^+ + 2e^-$ Cathode: $H_2O_2 + H_2SO_4 + 2e^- \rightarrow 2H_2O + SO_4^{2-}$

Overall: $2H_2O_2 + H_2SO_4 + 2KOH \rightarrow O_2 + 4H_2O + K_2SO_4$
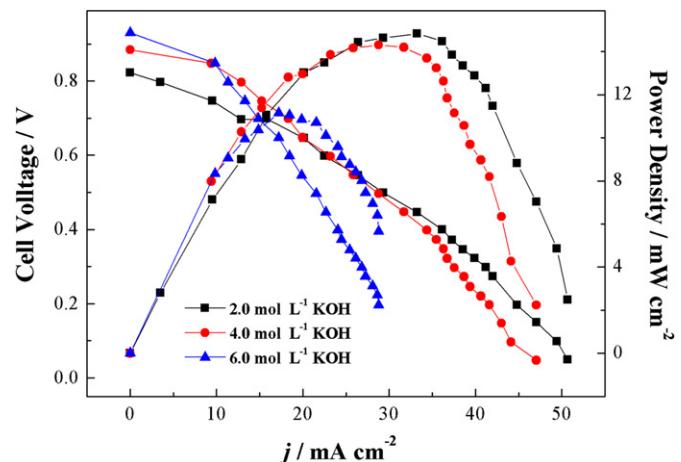
Fig. 2. Effect of KOH concentration in the anolyte. Anolyte: x mol L^{-1} KOH + 1.0 mol L^{-1} H_2O_2 (x = 2.0, 4.0 and 6.0). Catholyte: 2.0 mol L^{-1} H_2SO_4 + 2.0 mol L^{-1} H_2O_2. Flow rate: 10 mL min^{-1}. Operating temperature: 20 °C.

(i.e. the ratio of $[H^+]/[H_2O_2]$ is 2, which is the stoichiometric ratio in cathodic reaction, Fig. 1). As can be seen in Fig. 2, the DPPFC has an open circuit voltage (OCP) up to around 0.9 V, which is comparable with that of a hydrogen-fueled polymer electrolyte membrane fuel cell and certainly higher than that of a DMFC. The increase of KOH concentration resulted in a slight increase of the OCP, which is in good agreement with literature results [4,25]. However, the increases of KOH concentration from 2.0 to 4.0 mol L^{-1} did not lead to obvious enhancements in cell performance and a further increase in KOH concentration to 6.0 mol L^{-1}decreased performance. For example, the peak power density decreased from 14.8 mW cm^{-2} to 11.2 mW cm^{-2} when the concentration of KOH increased from 2.0 to 6.0 mol L^{-1}.

Fig. 3 shows the effect of the concentration of H_2O_2 in the anolyte on cell performance. The concentration of KOH in the anolyte was kept at 4.0 mol L^{-1} with the concentration of H_2O_2 changed from 0.5 to 2.0 mol L^{-1}. The catholyte was 2.0 mol L^{-1} H_2SO_4 + 2.0 mol L^{-1} H_2O_2. It is seen that the OCP is independent of the H_2O_2 concentration and reached 0.9 V. The peak power density increased with H_2O_2 concentration from 0.5 to 1.0 mol L^{-1}, however, decreased with the further increase from 1.0 to 2.0 mol L^{-1}. The peak power density with 1.0 mol L^{-1} H_2O_2 + 4.0 mol L^{-1} KOH was around 14.3 mW cm^{-2}, corresponding to a cell voltage of 0.5 V and a cell current density of 28.7 mA cm^{-2}. This performance is significantly higher than that reported in literature [3,4]. For example, Sanli et al. reported a DPPFC with a power density of 3.9 mW cm^{-2} at a cell voltage of 0.28 V and a current density of 14 mA cm^{-2}.

3.2. Effects of catholyte composition

Fig. 4 shows the dependence of DPPFC performance on the H_2SO_4 concentration in the catholyte. The concentration of H_2O_2 in the catholyte was fixed at 2.0 mol L^{-1} and the anolyte contained 1.0 mol L^{-1} H_2O_2 + 4.0 mol L^{-1} KOH. Clearly, the increase of H_2SO_4 concentration from 2.0 mol L^{-1} to 4.0 mol L^{-1} considerably reduced cell performance. When the concentration of H_2SO_4 increased from 2.0 to 4.0 mol L^{-1}, the OCP remains largely unchanged. The poor performance at high H_2SO_4 concentration is likely caused by the facilitated diffusion of H^+ from the cathode to anode crossing over the membrane. These protons will neutralize the OH^- resulting in a cell performance decrease.


Fig. 4. Effect of H_2SO_4 concentration in the catholyte. Anolyte: 4.0 mol L^{-1} KOH + 1.0 mol L^{-1} H_2O_2. Catholyte: x mol L^{-1} H_2SO_4 + 2.0 mol L^{-1} H_2O_2 (x = 2.0, 3.0 and 4.0). Flow rate: 10 mL min^{-1}. Operating temperature: 20 °C.

The effects of H_2O_2 concentration in the catholyte on cell performance was also investigated by fixing the concentration of H_2SO_4 at 2.0 mol L^{-1} and using 4.0 mol L^{-1} KOH + 1.0 mol L^{-1} H_2O_2 as the anolyte. The results are shown in Fig. 4. As can be seen, the variation of H_2O_2 concentration led to no changes in the OCP (0.9 V), but the cell performance was obviously improved by increasing the H_2O_2 concentration in the catholyte. The peak power densities at 0.5, 1.0 and 2.0 mol L^{-1} H_2O_2 are 9.2, 11.5 and 14.3 mW cm^{-2}, respectively. A further increase in H_2O_2 concentration beyond 2.0 mol L^{-1} will make H_2O_2 insufficient according to the cathode reaction stoichiometry (Fig. 1). Based on the results from Figs. 4 and 5, it can be concluded that the optimum composition of the catholyte is 2.0 mol L^{-1} H_2O_2 + 2.0 mol L^{-1} H_2SO_4, that is, the mole ratio of H_2O_2 and H^+ should be 1–2, which is the stoichiometric ratio of the cathode reaction.

3.3. Effects of temperature and flow rate

The effect of flow rate on cell performance is shown in Fig. 6. When the flow rate of both the anolyte and the catholyte is


Fig. 3. Effect of H_2O_2 concentration in the anolyte. Anolyte: 4.0 mol L^{-1} KOH + x mol L^{-1} H_2O_2 (x = 0.5, 1.0, 2.0). Catholyte: 2.0 mol L^{-1} H_2SO_4 + 2.0 mol L^{-1} H_2O_2. Flow rate: 10 mL min^{-1}. Operating temperature: 20 °C.
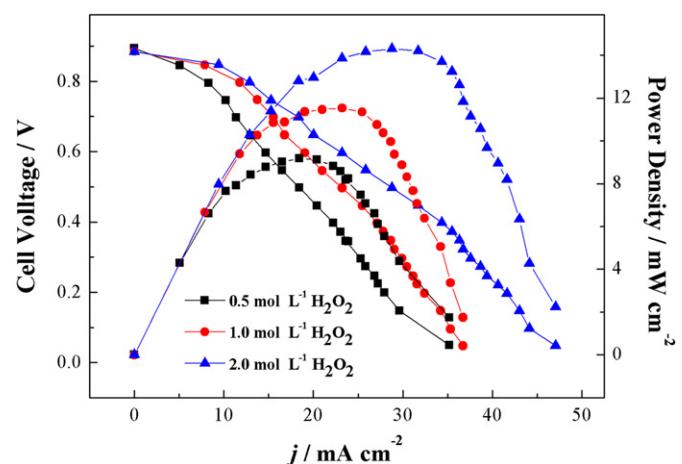
Fig. 5. Effect of H_2O_2 concentration in the catholyte. Anolyte: 4.0 mol L^{-1} KOH + 1.0 mol L^{-1} H_2O_2. Catholyte: 2.0 mol L^{-1} H_2SO_4 + x mol L^{-1} H_2O_2 (x = 0.5, 1.0 and 2.0). Flow rate: 10 mL min^{-1}. Operating temperature: 20 °C.
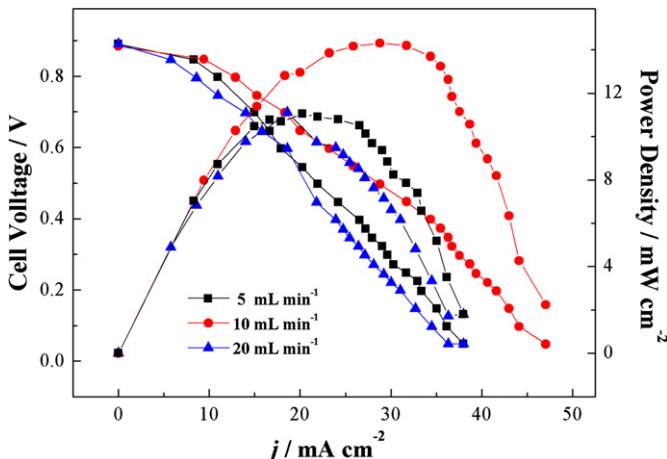
Fig. 6. Effect of the flow rate on the cell performance. Anolyte: 4.0 mol L^{-1} KOH + 1.0 mol L^{-1} H$_2$O$_2$. Catholyte: 2.0 mol L^{-1} H$_2$SO$_4$ + 2.0 mol L^{-1} H$_2$O$_2$. Flow rate: x mL min^{-1} (x = 5, 10, 20). Operating temperature: 20 °C.

Fig. 8. Stability test of the fuel cell. Anolyte: 4.0 mol L^{-1} KOH + 1.0 mol L^{-1} H$_2$O$_2$. Catholyte: 2.0 mol L^{-1} H$_2$SO$_4$ + 2.0 mol L^{-1} H$_2$O$_2$. Flow rate: 10 mL min^{-1}. Operating temperature: 40 °C. Current density: 45 mA cm^{-2}.

10 mL min^{-1}, the cell exhibited the best performance. The flow rate may have a controversial effect on the cell performance. Slow flow rates provokes crossover of hydrogen peroxide and H$^+$ through the Nafion® membrane more significant, since the contact time of acid and base solutions increases with the decrease in the slow rate. High flow rates implies that more H$_2$O$_2$ are supplied to the anode and cathode, and thus increase the H$_2$O$_2$ oxidation and reduction rate at the anode and cathode respectively [26]. However, it could also increase the hydrolysis rate of H$_2$O$_2$ at the anode and cathode catalyst surfaces leading to the cell performance reduction. So suitable flow rates could improve the cell performance.

Fig. 7 demonstrates the dependence of cell performance on operating temperatures. Clearly, cell performance considerably improved with increase in operating temperature. The peak power density reached 58.4 mW cm^{-2} corresponding to 131 mA cm^{-2} and 0.45 V at 60 °C. The higher performance at higher operating temperature can be attributed to the faster kinetics of both the anode and the cathode reactions and the higher electrolyte conductivity at higher temperatures. It should be pointed out that the increase of temperature will accelerate the chemical decomposition of H$_2$O$_2$, particularly in the anolyte, due to the instability of

H$_2$O$_2$ in alkaline medium. The decomposition of H$_2$O$_2$ results in a decrease in the utilization efficiency of H$_2$O$_2$. Therefore, there is a compromise between the cell performance and the utilization efficiency of H$_2$O$_2$. That is, the cell performance can be improved by operating at high temperature and/or using high concentration of H$_2$O$_2$, but at the expense of loss of H$_2$O$_2$.

3.4. Short-term stability test

A short-time discharge test at constant current was performed to check the stability of the DPPFC. The DPPFC was operated at a constant discharge current density of 45 mA cm^{-2} and at 40 °C. 4.0 mol L^{-1} KOH + 1.0 mol L^{-1} H$_2$O$_2$ and 2.0 mol L^{-1} H$_2$SO$_4$ + 2.0 mol L^{-1} H$_2$O$_2$ were continuously fed to the anode and cathode compartments, respectively, at a flow rate of 10 mL min^{-1}. Fig. 8 shows the dependence of cell voltage on operating time. The DPPFC was first left at the OCP for 3 min and then at 45 mA cm^{-2} for 1 h. It can be seen that the fuel cell has a stable OCV of 0.9 V and a working voltage of approximately 0.58 V at 45 mA cm^{-2} current load. During the 1 h test period, the cell voltage remained almost constant and 26 mW cm^{-2} power density was continuously generated. The excellent stability is due to the simple anode and cathode reactions involving no poisoning intermediates or products. As far as we know, such high DPPFC performance has not been previously reported.

4. Conclusions

We successfully demonstrated a high performance DPPFC using Pd/CFC electrode both as the anode and cathode, and H$_2$O$_2$ as both the fuel (in KOH) and the oxidant (in H$_2$SO$_4$). The DPPFC displayed a stable OCP of ∼0.9 V, comparable with a hydrogen-fueled PEMFC and much higher than that of a DMFC. A peak power densities of 14.3 mW cm^{-2} at 20 °C and 58.4 mW cm^{-2} at 60 °C were achieved. The cell performance depends upon the concentration of KOH, H$_2$SO$_4$ and H$_2$O$_2$, the operating temperature and the flow rate of the anolyte and catholyte. Better performance was obtained using 4.0 mol L^{-1} KOH + 1.0 mol L^{-1} H$_2$O$_2$ as the anolyte and of 2.0 mol L^{-1} H$_2$SO$_4$ + 2.0 mol L^{-1} H$_2$O$_2$ as the catholyte. The results indicated that DPPFC is a promising new type of fuel cell with a great application potential.
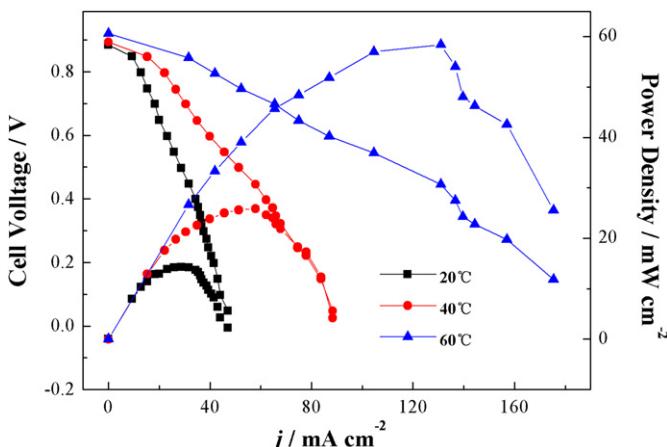
Fig. 7. Effect of operating temperature on the cell performance. Anolyte: 4.0 mol L^{-1} KOH + 1.0 mol L^{-1} H$_2$O$_2$. Catholyte: 2.0 mol L^{-1} H$_2$SO$_4$ + 2.0 mol L^{-1} H$_2$O$_2$. Flow rate: 10 mL min^{-1}.

Acknowledgments

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